A Stable σ-Allyl Organopalladium Compound. *X*-Ray Structure of the Dimeric Complex$(C_8H_{11}PdCl)_2$

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Summary: The allyl palladium complex obtained from cyclo-octa-1,5-diene is shown to be a σ-allyl complex.

Reaction of triethylamine with (cod)$PdCl_2$ (cod = cyclo-octa-1,5-diene) complex affords a dimeric compound $(C_8H_{11}PdCl)_2$, to which the π-allyl structure (**1**) was assigned on the basis of i.r., Raman, and molecular weight data.[1] We report here an *X*-ray analysis which indicates that this compound has in fact the σ-allyl structure (**2**), at least in the solid state.

Crystal data: $C_{16}H_{22}Cl_2Pd_2$ is rhombohedral, $a = 27{\cdot}155(7)$, $c = 6{\cdot}669(6)$ Å (hexagonal axes); space group $R\bar{3}$; $D_m = 1{\cdot}730$ g cm^{-3}; $D_c = 1{\cdot}747$ g cm^{-3} for $Z = 9$. The Figure corresponds to the configuration of one dimer. The

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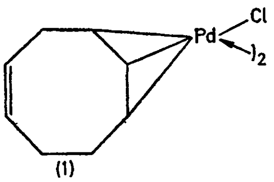
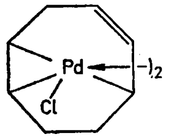
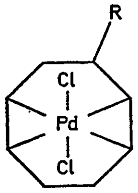
X-ray structural analysis was based on 731 unique non-zero intensities (Mo-K_{α}, Philips PW 1100 four-circle diffractometer). The structure was solved by Patterson and Fourier procedures and refined by full-matrix least-squares with anisotropic temperature factors. At the present state of refinement the R factor is 0·051.



(1)



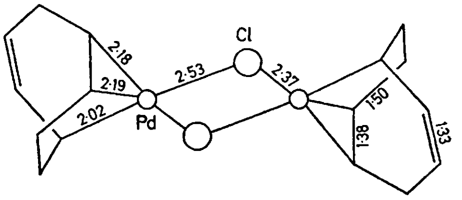
(2)



(3)

The X-ray data clearly show the well known larger *trans*-influence[2] of the σ C–Pd bond, compared with the π C–Pd bond, as shown by the corresponding *trans*-Pd–Cl bond lengths (2·53 and 2·37 Å respectively).

Usually allyl-transition metal complexes in solution exhibit a dynamic equilibrium between the π-allyl and the σ-allyl structure,[3] but the crystalline compounds very often possess the π-allyl structure; the σ-allyl compounds are postulated as reaction intermediates and can be observed by ^{1}H n.m.r. spectroscopy.[4] To our knowledge compound (**2**) is the first reported example of a crystalline σ-allyl derivative of palladium.[5] In structure (**2**) the metal is apparently preferentially bound by a σ-bond plus a chelating double bond rather than by a π-allyl bond. This effect should not necessarily be restricted to palladium, and it is conceivable that the cationic iron and ruthenium complexes derived from (cod) and described by Cotton *et al.*[6] as π-allyl systems, actually are σ-allyl systems.



FIGURE

Reactions of compound (**2**) with electrophiles (HCl, MeCOCl) lead to compounds (**3**; R = H, MeCO),[1] the formation of which can be explained by an S_E2' type mechanism, as found with more usual σ-allyl organometallic compounds derived from magnesium or tin.[7]

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